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## MICRONUTRIENT AVAILABILITY

### Chemistry and Availability of Micronutrients in Soils

FRANK G. VIETS, Jr.  
U. S. Department of Agriculture,  
Fort Collins, Colo.

Recent developments in the chemistry and availability of micronutrients are difficult to generalize because of the great diversity in their chemical properties, their reactions with soil, and the plant roots' ability to absorb them from the soil. Five chemical pools for each cation are postulated based on solubility, exchange reactions, and chemical form. The micronutrient anions cannot be separated into equally definite pools. These pools are discussed in relation to research on soil tests and significance to plant absorption.

PUBLIC INTEREST in the mineral micronutrients is at an all time high and will undoubtedly increase as more instances and kinds of deficiencies are brought to light. The correction of a micronutrient deficiency in vegetation or of a malady in livestock by the application of a microelement to soil or to foliage—often only a fraction of an ounce of the element to an acre—offers some of the most spectacular instances of man's domination of nature.

Since about 1860 when Fe was shown to be needed by green plants, the list of essential micro or trace elements has

grown steadily as experimental techniques and methods for removal of trace element impurities from chemicals and water improved. Micronutrient cations required by higher plants now include Fe, Cu, Zn, and Mn. Cobalt is essential for legume bacteria in the fixation of nitrogen from air and, hence, is basic to our agricultural economy. Some species of plants require or are benefited by Na, also. The list of micronutrient anions now includes B, Mo, and Cl. Interest in micronutrients does not stop at what plants alone need, but includes those additional ones needed by animals and

not supplied in adequate amounts by forage and grain. Additional ones are Co for microbial synthesis of vitamin B<sub>12</sub> (which contains Co) in the gut of ruminants; I for the thyroid hormone, thyroxine; Se for prevention of white muscle disease; and possibly Ba, Sr, and Br (7).

The only property that the micronutrients have in common is that plant and animal requirements for them are small in contrast to their requirements for the macroelements. However, even within the trace group for plants, large differences in requirements occur (25).

For example, 0.5 p.p.m. Mo in most plants is adequate, but Fe must be present in concentrations of about 100 p.p.m. on a dry-weight basis. Each micronutrient has its own specific functions in the enzyme systems of organisms, but knowledge of these functions only emphasizes their importance and helps little in understanding their chemistry and availability in the soil.

The micronutrient cations in their available state in the soil generally occur in the divalent form (Fe may also be trivalent) and so are subject to strong adsorption on the negatively charged clay and humus. The micronutrient anions show more diversity in their adsorption reactions. Chloride displays negative adsorption. Borate and molybdate are adsorbed or precipitate in some soils and not in others.

To bring some order into a discussion of current research on microelements that have so little in common, the concept of the chemical pool based on exchange and solubility reactions has considerable merit.

### The Concept of Chemical Pools

For at least a century, soil has been extracted with water, salt solutions, acids, and bases. The amount extracted could vary from none for some elements like Zn when water was used to almost the total amount in the soil when strong acids and heat were used. In other words, the amount of an element extractable from the soil made a continuous array between none and almost all if enough reagents and variations in procedures were used.

The problem is one of making chemical and physiological sense out of the soil-plant system when so little is really known about the physical chemistry of the micronutrients in the soil system and the plant's reactions to it. The chemical pool is simply the amount of an element in a given state that can be estimated by extraction and isotopic dilution techniques. The chemical pool of each element is assumed to have the attributes of concentration, size, turnover rate, and equilibrium with other pools of that element.

**Micronutrient Cation Pools.** The generalized pools for the cations based largely on exchange and chelation reactions are depicted in Figure 1. This diagram is not a spatial representation of the pools as they occur in soil, but is rather a convenience for understanding the solubility and availability of the micronutrient cations. At the center is water-soluble pool A containing nonadsorbed ions and ions adsorbed on suspended colloids that are estimated on a displaced soil solution or an aqueous extract of the soil using various soil-to-water ratios—i.e., 1:1 and 1:5. The effect of the soil's own pH (or exchange-

able Al<sup>+3</sup>), redox potential, and concentration of other ions on the ion being considered are variable factors affecting this pool. This pool is usually small or almost nonexistent for Zn and Cu, and very small (< 1 p.p.m.) for Mn and Fe in well aerated neutral soils. Poor aeration (low redox potential) coupled with low pH can markedly increase the size of this pool for Mn and Fe, but has little effect on Zn or Cu. This pool can be increased for a time in very sandy soils with Cu, Zn, or Mn fertilization.

Next is pool B obtained by extracting the soil with weak cation and anion exchangers, neutral 1*N* ammonium acetate being commonly used. This pool usually includes water-soluble pool A and so is shown as a concentric circle around A. Pool B is larger than A but for Zn and Cu is still small except on some soils well supplied with these elements. Exchangeable Mn of pool B is frequently used for predicting adequacy of Mn (23, 27).

Pool C contains cations that can be replaced only by the mass action of cations with similar affinities for the adsorbent or by extraction with chelating agents. Abundant evidence obtained in the last 10 years confirms the existence of such a pool in which micronutrient cations are absorbed with great affinity by clay and humus of the soil. Pool C, as usually determined, includes pools B and C, but it can be estimated separately. Some examples of evidence for this pool are: Hodgson (10) found that Ca saturated montmorillonite absorbed Co<sup>+2</sup> in the presence of 0.1*N* CaCl<sub>2</sub>. Part of this absorbed Co could be desorbed by Cu<sup>+2</sup> or Zn<sup>+2</sup>, but not by Ca<sup>+2</sup>, Mg<sup>+2</sup>, or NH<sub>4</sub><sup>+</sup>. He called these reactions of Zn<sup>+2</sup> and Cu<sup>+2</sup> for Co<sup>+2</sup> specific exchange reactions and the Co, chemisorbed. A fraction of the absorbed Co<sup>+2</sup> could not be displaced even with 2% acetic acid and presumably became part of the crystal lattice of the clay (pool D). Miller and Ohlogge (17) found a fraction of added Zn in soil that could be removed by a 2*N* KCl-CuCl<sub>2</sub> solution or by aqueous extracts of organic materials, but could not be removed by 2*N* KCl. Walker and Barber (27) found a fraction of Mn, which they termed chelated, in 12 Indiana soils that could not be extracted with 1*N* neutral ammonium acetate but could be extracted with 0.03*N* Zn(NO<sub>3</sub>)<sub>2</sub>.

Chelating agents like EDTA appear to measure this pool of strongly adsorbed and chelated or complexed cations, and may dissolve some inorganic precipitates of Zn, Fe, Cu, and Mn as oxides, hydroxides, phosphates, and carbonates on fertilized soils. Shaw and Dean (22) found that 1*N* neutral ammonium acetate extracted no Zn from three soils but that the two-phase system of neutral 1*N* ammonium acetate and CCl<sub>4</sub>

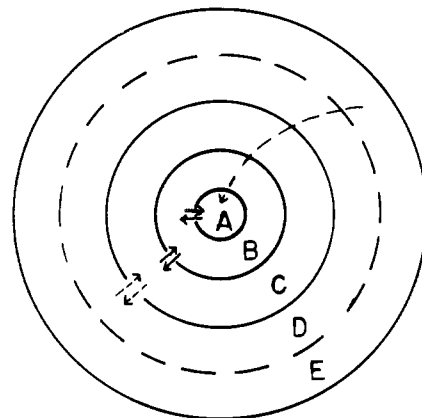


Figure 1. The postulated pools of micronutrient cations in soil

- A. Water soluble
  - B. Cations exchangeable by a weak exchanger like NH<sub>4</sub><sup>+</sup>
  - C. Adsorbed, chelated, or complexed ions exchangeable by other cations possessing high affinities for exchange sites or extractable with stronger chelating agents
  - D. Micronutrient cations in secondary clay minerals and insoluble metal oxides
  - E. Cations held in primary minerals
- The pools collectively hold the total amount of that element in the soil

containing dithizone extracted from 0.6 to 4.3 p.p.m. Epstein and Stout (7) previously used this two-phase system for quantitative removal of added Zn<sup>65</sup> from bentonite. Studies by Viro (26) showed about 90% recovery of Zn and Cu by ammonium EDTA at pH 7 when Zn and Cu were added at the rate of 1 p.p.m. each to five acidic soils, whereas neutral 1*N* ammonium acetate recovered only 41% of the Zn and 11% of the Cu. Removal of Zn from soils with EDTA is consistently higher than the removal with ammonium acetate (13, 24). Chelating agents vary enormously in their ability to extract ions depending on the stability constant of the chelate and the cation (16). To estimate pool C with chelates, ones with high stability constants must be used.

Pools A, B, and C are undoubtedly in reversible equilibrium with one another as indicated by the double arrows in Figure 1, with equilibrium being established quickly. Micronutrient cations in these pools appear to be readily available to plants. Pool C is of the greatest significance to plants because of its size.

Around these three central pools of Figure 1 are the secondary minerals of pool D and the primary minerals of pool E. They are separated by a broken line because of the difficulties of separating them by chemical methods. The secondary minerals are precipitates that are highly resistant to weathering, and the layer silicate clays that may contain micronutrient cations in various degrees of isomorphous substitution for Al and Si and by occlusion. The clays, in addi-

tion to providing adsorption sites for pools *B* and *C*, are probably sinks in which the cations become nonextractable and probably unavailable to plant roots. Hodgson (70) has shown that a portion of the Co added to montmorillonite cannot be displaced. That portion of the Zn added to a soil that cannot be extracted with 0.1N HCl and that increases with time (3, 4) probably enters a clay lattice. The equilibrium between pool *D* and pools *C*, *B*, and *A* is established slowly and may be largely through the solution phase of pool *A*, although contact migration is a possibility (17).

Pool *E* contains the primary minerals of the soil. By definition, this pool is not in reversible equilibrium with the other pools. This pool probably releases its cations to the other pools through pool *A*, although contact migration cannot be ruled out. Pool *E* may be large in arid and semiarid, unweathered soils but may be small or have disappeared in highly weathered soils. The primary minerals in weathering probably release a greater proportion of their micronutrient cations in available form than do the highly stable secondary minerals of pool *D*.

All pools added together constitute the total content of the element in the soil. Total content is of little value in predicting sufficiency or deficiency of a micronutrient except where the total content is very low.

The ubiquitous H ion is difficult to fit into the postulated pools as an extracting or replacing agent. This is not too surprising since in analytical schemes its concentration may vary over seven or eight orders of magnitude—i.e., pH 8 or 9 to 1. Hydrogen ion is highly competitive in adsorption reactions depending on its concentration. At neutrality, it measures only pool *A*. As its concentration is increased, it extracts pool *B*, then *C*, and finally at higher concentrations it may attack pools *D* and *E*. Strong acids at high temperature may extract virtually all pools. It dissolves, neutralizes, and destroys adsorbing surfaces, making interpretations of exchange relationships difficult. It is unfortunate that acids have been the basis of so many extraction procedures.

The pools shown in Figure 1 are arbitrary but recognizable. Further research will show the identity of these pools and the equilibrium and rates of equilibrium that exist among them. They are presented here to facilitate, at least in a qualitative way, a better understanding of the micronutrients.

Fitting organic matter and humus into a scheme of pools involves considerable speculation. Return of crop residues and organic manures to the soil where they are broken down by microbes adds micronutrients to the system. Whether the micronutrient

cations are released into pool *A* or whether they are retained adsorbed or complexed on surfaces of materials that eventually become humus is not known. When organic decomposition occurs in soil, water-soluble Mn can increase in pool *A*, but this may be due to reduction because of poor aeration and a consequent shift in equilibria among pools *A*, *B*, and *C*. In many soils, humus or organic matter contributes appreciably to the cation exchange capacity. This contribution is about 2.8 meq. per 100 grams for each change of 1% in organic matter (20) for Ramona sandy loam in southern California for ions exchangeable with ammonium acetate, but this relationship is different for organic matter of different soils. Such information is not available for micronutrients. However, much evidence shows that humus is active in complexing or chelating micronutrients. Humus may be the absorbent of greatest importance for pool *C* in many soils. Bremner *et al.* (5) suggested that the micronutrient cations may be responsible for stabilizing humus in soil.

Management and fertilizer practices and soil formation can be understood more readily through the pool approach. For example, poor soil aeration, especially if accompanied by low pH, greatly expands the water-soluble pool *A* of  $Mn^{+2}$  and  $Fe^{+2}$  at the expense largely of the oxides in pool *D*, although the other pools may be affected too. Good aeration or increase in the redox potential has the opposite effect. Acidification of a soil increases the availability and the amount of Zn free to move in the soil water. This Zn may come largely from the *B* and *C* pools. Podzolic soils which are highly acidic in the surface show an impoverishment of Zn and Cu in the *A* horizon and their accumulation in the *B* horizon (28). Liming a soil has an effect opposite to that of acidification; micronutrient cations in the soil solution, especially  $Mn^{+2}$  and  $Fe^{+2}$ , virtually disappear. However, this does not mean that liming induces micronutrient deficiencies, although overliming of some acid soils does do this. When a water-soluble cation like  $Zn^{+2}$  from  $ZnSO_4$  is added to a soil, it quickly migrates from the water-soluble pool *A* through the weakly exchangeable pool *B* to the *C* pool where it can be extracted with 0.1N HCl (78). Finally, much of it migrates slowly to an unidentified secondary mineral of pool *D* where it is nonextractable with 0.1N HCl and becomes unavailable to plants (4).

**Micronutrient Anion Pools.** In contrast to cation pools, those for anions are much less well defined. Chloride is an essential element for plants (6), but deficiency in the field is unknown. It occurs in the primary minerals of soil (pool *E*), and because of its negative ad-

sorption in soils  $Cl^-$  remains in pool *A* when added in fertilizers or irrigation waters. In excess amounts, it can produce specific injury to some crops and contribute to a general salinity problem.

Boron occurs in pool *E* largely as the primary mineral tourmaline. Much of the boron in soils is complexed with humus probably in pool *C*, where its release to plants is presumably dependent on soil moisture affecting root growth and microbial activity. This explanation has not been proved, however. Soluble borate added to soil is weakly adsorbed, the adsorption following a Langmuir isotherm (2, 9) and increasing as pH increases (79). Boron fixation is also dependent on clay content. Soluble borate added to soils remains largely in pool *A* where it can be toxic to sensitive species if too much is applied. It accumulates in some southwestern arid soils and care in its use is essential where drainage water is reused.

Molybdenum occurs in all the postulated pools. Adsorbed  $MoO_4^{-2}$  is replaceable by oxalate, phosphate, and hydroxyl ions. Liming increases the availability of Mo and increases the size of water-soluble pool *A* (74). Under acid conditions, it precipitates with the oxides of iron and to a lesser extent with aluminum and titanium (21) of pool *D*. Water-soluble molybdate added to soil remains largely in pool *A* so that extremely small amounts added to a soil will correct a deficiency. Poorly drained granitic soils of California and Nevada accumulate so much available molybdate that the grasses and clovers are toxic to livestock (75).

#### Nutrient Availability and Pools.

The solution theory holds that any ion in the soil solution (pool *A*) is available to the plant if the root is capable of absorbing it. Any ion in the pools other than *A* must pass into solution and move to the plant root by diffusion or mass flow of water before being absorbed. Root extension into unexplored zones shortens the distances enormously. In the solution theory,  $H^+$  produced by roots either directly or from  $CO_2$  reaction with water is postulated as a displacing agent between the solid and solution phase. This action of  $H^+$  is not fundamental to the theory, however. A corollary of the solution theory is the possibility that plant roots or microbes of the rhizosphere produce chelating organic acids that can solubilize cations and transfer them to pool *A*. If solution (pool *A*) is the only operative mechanism of transport to the plant root, then pool *A* and the rate of its equilibration with the other pools is extremely important.

The contact theory (72) holds that an ion can pass directly from the adsorbed state on the solid phase to the root in exchange for an adsorbed  $H^+$

or other ion without going through the solution phase of pool *A*. The contact theory has appeal as an adjunct to the solution theory in at least qualitatively explaining how plants can absorb elements from extremely insoluble compounds like  $MnO_2$ ,  $Fe(OH)_3$ ,  $CuS$ , and  $Zn$  compounds soluble only in 0.1*N* HCl, particularly when they are highly divided. In other words, plants can get ions from soils where there are no measurable *A* and *B* pools and sometimes *C* pools.

Although the solution theory is well established in plant nutrition, it has not yet been established as adequate to explain all soil-root-uptake phenomena. Likewise, the contact theory has not been established as an essential mechanism. Certainly, "microregion" phenomena, as Glauser and Jenny (8) put it, are involved in the mechanism of uptake of micronutrient cations from the solid phase holding pools *C* and *D*. These several theories are recounted to illustrate the state of uncertainty that exists in understanding this vital bridge in soil-plant micronutrient relations.

#### Fertilizer Practice and the Concept of Pools

The microelements added in fertilizers to soils react with them and end up in one of the postulated pools where they may be available, or unavailable, or even toxic to plants. For example, addition of soluble inorganic iron compounds for correction of iron chlorosis on calcareous soils is ineffective partly because they go so quickly from pools *A* through the others to *D*. Iron contained in some soluble organic chelates added to soil remains in pool *A* long enough to be an effective, but generally expensive, control. Water-soluble  $Zn$  compounds generally revert to pool *C* so fast that compounds that are soluble in 0.1*N* HCl like  $ZnO$  and  $ZnCO_3$  are just as good for correction of  $Zn$  deficiency as  $ZnSO_4$  (3). In a season, the plant can get only 2 or 3% of the  $Zn$  that is added. This fixation can be tolerated only because  $Zn$  is cheap. To slow down this rapid reversion of micronutrient cations to pools of lower solubility, placement of water-soluble materials in bands or their incorporation in frits or glasses so that there will be slow release to pool *A* is tried with varying degrees of success. To prevent too much accumulation of an element like boron in pool *A* where it can be leached or be toxic to sensitive plants, the use of boron in frits, glasses, and relatively insoluble borates is practiced.

#### Soil Testing and the Concept of Pools

In their search for better methods to characterize the fraction of nutrients in the soil available for plant uptake, soil

chemists have changed their methods as their concepts of soil-plant relationships changed. Through the first two decades of this century, the chemist's interest was on total analysis of the soil—an estimate of the total pool. This approach gradually lost favor as marked discrepancies between total content and availability were noted. A modern example is the extensive zinc deficiency now noted on many western irrigated soils that contain average to high amounts of total  $Zn$ . This era of total analysis was followed with one of emphasis on the solution that could be displaced from the saturated soil with water or air. Extraction of the soil with water was a kindred attempt to measure pool *A*. For the micronutrient cations, these procedures generally failed because pool *A* was small or practically nonexistent except in rare circumstances. For weakly adsorbed boron, extraction with hot water is now standard practice in soil testing. Water extraction of nitrate, frequently after an incubation procedure to enlarge the pool from organic nitrogen decomposition, is also an estimate of pool *A*. For the cations, interest shifted to estimating the exchangeable cations with ammonium acetate and other weak displacing cations. Pools *A* and *B* were thus combined. In the 1930's, there was much interest in attempting to imitate the solvent action of plant roots by using dilute acidic solutions and  $CO_2$ -charged water for extraction.

The current trend in estimating availability of micronutrient cations is to extract the soil with more vigorous reagents in an attempt to establish the best possible correlation of extractable cation with actual plant uptake. In some cases, this research can be interpreted in relation to the pools discussed here. Walker and Barber (27) estimated the exchangeable  $Mn$  of 12 Indiana soils with ammonium acetate (pools *A* and *B*) and with  $Zn(NO_3)_2$  (pool *C*). The exchangeable  $Mn$  was correlated ( $r^2 = 0.81$ ) with the plant uptake of  $Mn$ , but the correlation could not be improved by the inclusion of pool *C*. The exchangeable  $Mn$  was highly correlated ( $r^2 = 0.74$ ) with the difficultly exchangeable  $Mn$  extracted by  $Zn^{+2}$ . Thus, the  $Mn$  of pools *B* and *C* appears to be in reversible equilibrium, and an estimate of pool *B* alone was sufficient. Tucker and Kurtz (24) reported high correlations among the amounts of  $Zn$  extractable from 14 soils with various reagents and with  $Zn$  extracted by *Aspergillus niger*. This is evidence that equilibrium among the pools is rapidly re-established.

Many examples of this approach to understanding of the availability of microelements in relation to their extractability could be cited, but the data are often difficult to interpret in relation to

the concept of pools. Certainly more attention should be paid to the relationship of absolute amounts of nutrients in the pools and plant uptake, and not stop at establishment of correlations and regression equations.

#### Discussion

The concept of pools differing in size and turnover rates has been applied to nitrogen in soils and ecosystems, and to forms of  $N$  and  $P$  in oceans. Such concepts have equal usefulness in understanding the chemistry of soil and the form and placement of fertilizers into it for maximum effectiveness.

The pools of micronutrients in soils can now be defined, at best, only very qualitatively because of lack of knowledge of the chemistry of the system and the plant roots' behavior in relation to that system. This complexity should not discourage forging ahead toward an understanding of the chemical pools involved.

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## MICRONUTRIENT SHORTAGES

# Micronutrient Deficiencies in the United States

KERMIT C. BERGER  
 Soils Department,  
 University of Wisconsin,  
 Madison, Wis.

The Trace Element Committee of the Council on Fertilizer Application has listed the known micronutrient deficiencies, by crop, as reported by research workers in each of the 50 states. The results show these deficiencies to be widespread with boron being reported as deficient in one or more crops in 41 states, copper in 13, manganese in 25, molybdenum in 21, iron in 25, and zinc in 30. Boron-deficient alfalfa was reported in 38 states, and zinc-deficient corn in 20. Crop needs for micronutrient elements are expected to continue to increase in the future. The areas of micronutrient deficiencies within the state are generally quite limited and are not nearly as extensive as are the areas of deficiencies of nitrogen, phosphorus, and potassium. Promiscuous use of micronutrient elements as a soil application should not be encouraged because of the dangers of building up toxic quantities of these elements.

THE RECOGNITION of the need of micronutrient applications to crops becomes greater each year because more research is being done on micronutrients, soils are becoming more depleted in them, and crop yields are increasing throughout the U. S. For example, in Wisconsin, copper and zinc were sufficient at a 100-bushel level of corn. Increasing major nutrient element fertilization increased the yield about 25 bushels per acre. The addition of 2 pounds of copper oxide and 10 pounds of zinc sulfate further increased the yield by 16 bushels.

The Trace Element Committee of the Council on Fertilizer Application surveyed the micronutrient needs by crops in the U. S. The results obtained for boron, copper, iron, manganese, molybdenum, and zinc are presented here. All 50 states reported in answer to a questionnaire. The results of the survey listing the micronutrient deficiencies by crop for each state are given in Figures 1 to 6.

For the most part, areas of micronutrient deficiencies within the state are too widely scattered to be delineated. However, in some instances, deficiencies are relatively isolated to a few soil

types and are well defined. In some states, peat and muck soils are deficient in one or more of the micronutrient elements for all crops grown. A general recommendation is usually given for all vegetable crops on these soils.

### Boron

Boron deficiencies, reported in 41 states, are the most widespread of all micronutrient deficiencies (Table I). States having boron deficiency are shown in Figure 1. Alfalfa, reported boron deficient in 38 states, leads all crops for all micronutrient deficiencies reported (Table II). Boron deficiencies

occur largely in more humid regions of the country and are not reported in arid regions of low rainfall where boron contents of soils and waters are high.

Table I. States Reporting Micronutrient Deficiencies in One or More Crops

Micronutrient Deficiency	Number of States
Boron	41
Copper	13
Iron	25
Manganese	25
Molybdenum	21
Zinc	30

Table II. Extent of Micronutrient Deficiencies in United States<sup>a</sup>

Crop	States	Crop	States
BORON			
Alfalfa	38	Corn	3
Beet	12	Fruit trees	3
Celery	10	Grasses	3
Clover	13	Onion	7
Cruciferae	25	Small grains	4
Fruit trees	21	MANGANESE	
IRON			
Bean	5	Bean	13
Corn	3	Corn	5
Fruit trees	11	Fruit trees	9
Grasses	7	Small grains	10
Shade trees	7	Spinach	8
Shrubs	11	ZINC	
MOLYBDENUM			
Alfalfa	13	Bean	7
Clover	6	Corn	20
Cruciferae	9	Fruit trees	12
Soybean	3	Nut trees	10
		Onion	4
		Potato	3

<sup>a</sup> Deficiencies also observed on many other crops but with less frequency.